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**Title: Magnesia-Calcia-Based Refractory**

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SPECIFICATION

**Title of the Invention**

Magnesia-calcia-based refractory

**Claims**

(1) A magnesia-calcia-based refractory characterized by being a refractory that contains 20-95% by weight of magnesia and 80-5% by weight of calcia as the refractory aggregate and by 20-80% by weight of the refractory aggregate being constructed of spherical particles.

(2) The refractory of Claim 1 that contains 0.5-5 parts by weight of aragonite-type calcium carbonate per 100 parts by weight of the refractory aggregate.

**Detailed Explanation of the Invention**

Industrial field of utilization

The present invention relates to a magnesia-calcia-based refractory with excellent spalling resistance.

Prior art and problems therein

Dolomite-based refractories have been widely used as the lining for various types of furnaces such as rotary furnaces, basic steelmaking furnaces, and cement rotary kilns. The appearance of refractories with better spalling resistance, thermal impact resistance, and the like has been demanded recently, however, as more rigorous operating conditions such as larger furnace size, higher tapping temperature, and shorter blow time have come to be used.

Basic refractories made mainly of magnesia (referred to hereinafter as MgO) have been developed in response to this situation. Although these refractories have excellent resistance to melting loss by highly basic slag, their major drawback is their inferior spalling resistance. Specifically, since the reactivity between MgO and slag is low, the slag penetrates to the interior of the brick that has a temperature corresponding to the melting point of the slag and loosens the crystal structure of the MgO crystals (periclase) present in the part penetrated. Physical differences (such as in thermal swelling coefficient, porosity, and strength) develop as a result between the parts penetrated and the parts not penetrated when the temperature of the brick drops and spalling tends to occur. Also, since MgO has a high thermal swelling coefficient, spalling also tends to occur due

to differences in the swelling of the brick to the inside of the furnace (high-temperature side) and the back side (low-temperature side). Therefore, thermal spalling and structural spalling develop in the brick due to a combination of various factors such as the action of the slag, heat warping caused by the construction of the furnace body, and the use cycle of the furnace (repeated heating and cooling) in MgO-based brick. The brick gradually detaches from the furnace body and the furnace eventually becomes unusable.

MgO-calcia (CaO)-based refractory brick that combines zirconia (more preferably stabilized zirconia) has been devised to resolve the aforementioned drawbacks of MgO-based brick (see Japanese Kokai Patent No. Sho 49-96005). In this brick, the slag that has penetrated to the interior of the brick and the zirconia react near the surface of the brick, thereby raising the viscosity of the slag. This is said to prevent further penetration of the slag and to improve the structural spalling resistance. However, this refractory brick offers almost no improvement of the thermal spalling resistance.

MgO-CaO-based refractories that combine raw materials such as dolomite and CaO with an MgO raw material have also been developed and are used frequently. Such refractories have high strength, but inadequate spalling resistance, thermal impact resistance, and the like. In particular when used as a lining material for cement rotary kilns and such, a coating layer made from cement components is usually formed on the surface of the refractory near the calcining zone and can be expected to lengthen the life of the refractory. In actuality, however, the coating layer is repeatedly desorbed violently by the rotation of the kiln and such, exposing the refractory surface to severe thermal impact and leading to spalling.

## Problems to be resolved by the invention

The present inventors discovered as a result of various studies conducted in view of the present state of the prior art as described above that the problems of magnesia-calcia-based refractories are essentially resolved or greatly diminished by using a specific quantity of spherical basic refractory aggregate particles.

Specifically, the present invention provides the following magnesia-calcia-based refractory.

(1) A magnesia-calcia-based refractory characterized by being a refractory that contains 20-95% by weight of magnesia and 80-5% by weight of calcia as the refractory aggregate and by 20-80% by weight of the refractory aggregate being constructed of spherical particles.

(2) The refractory of (1) above that contains 0.5-5 parts by weight of aragonite-type calcium carbonate per 100 parts by weight of the refractory aggregate.

Known basic refractory materials that contain MgO and/or CaO can be used as the refractory aggregate employed in the present invention. Concrete examples include magnesia clinker, dolomite clinker, and lime clinker. Magnesia clinker includes natural magnesia clinker, seawater magnesia clinker, and electrolyzed magnesia clinker. Dolomite clinker includes natural dolomite clinker, synthetic dolomite clinker, and electrolyzed dolomite clinker.

In the present invention, 20-80% by weight (simply referred to hereinafter as %) of the total quantity of the refractory aggregate raw material is constructed of spherical particles and the remainder is non-spherical particles. Ordinary basic refractory aggregate raw materials contain spherical particles, but the content is far less than 20%. When stress is applied to the magnesia-calcia-based refractory of the present invention that contains a specific amount of spherical particles, the spherical particles move without intertwining among themselves and the refractory deforms. The stress consequently does not concentrate in any part of the refractory and spalling such as detachment of the working surface layer or destruction by pressure in the joint does not occur. The anti-spalling effect is inadequate when the quantity of spherical particles is less than 20%. On the other hand, the strength of the refractory decreases when the quantity exceeds 80%.

The spherical particles are not particularly restricted as long as they are rounded, not angular, particles. Examples include true spherical, flat spherical, and elliptical spherical particles. The spherical particles can be obtained by selecting them out from the refractory aggregate. Or, they can be produced by an ordinary method such as melt spraying or grinding. The particle diameter of the spherical particles is not particularly restricted, but is preferably about 1/3 or less of the minimum thickness of the refractory in consideration of the strength of the refractory. For example, when the refractory of the present invention is used in a rotary furnace, the particles should usually be about 50 mm or less, preferably about 5-50 mm.

On the other hand, ordinary refractory aggregate raw material that is not spherical can be used as the non-spherical particles. Its particle diameter is not particularly restricted, but should usually be about 10 mm or less, preferably about 5 mm or less.

Together with the aforementioned specific quantities of spherical and non-spherical particles being used in the present invention, the MgO content in the refractory aggregate raw material is

adjusted to 20-95% by weight (simply referred to hereinafter as %) and the CaO content to 80-5%. The slaking resistance becomes inadequate and the slag melting loss resistance drops when the MgO is less than 20%. On the other hand, the spalling resistance and resistance to slag penetration decrease when the MgO exceeds 95%.

Aragonite-type calcium carbonate should also be added to the refractory of the present invention to further improve the spalling resistance. Aragonite-type calcium carbonate is converted into calcite-type at approximately 330-480°C during calcining of the refractory and undergoes sudden volumetric swelling. A large number of microcracks develop in the refractory. According to research conducted by the present inventors, these microcracks actualize a preventative effect against stress propagation during use of the refractory and are very effective in preventing the expansion of cracks caused by thermal spalling. This remarkable effect in the present invention is obtained only when aragonite-type calcium carbonate is used. For example, when refined calcium carbonate (calcite-type $CaCO_3$) was used instead of aragonite-type calcium carbonate, spherical spaces that had no preventative effect against crack expansion formed to an excess and no improvement of the spalling resistance was found.

Either natural products obtained, for example, from sea shells, coral, and the like and synthetic products can be used as the aragonite-type calcium carbonate. These may be used in mixture if necessary. The amount of aragonite-type calcium carbonate combined is usually 0.5-5 parts by weight (simply referred to hereinafter as parts) per 100 parts of the refractory raw material. Too few microcracks develop in the brick and the improvement of the spalling resistance is inadequate when the amount of aragonite-type calcium carbonate combined is less than 0.5 part. On the other hand, the structure becomes porous and the refractory property of the brick declines when it exceeds 5 parts. Although the particle diameter of the aragonite-type calcium carbonate is not particularly restricted, it is usually about 0.5-10 mm, more preferably 1-3 mm. The development of microcracks tends to decrease when the particle diameter of the aragonite-type calcium carbonate is less than 0.5 mm. Porosity caused by the development of cracks other than microcracks advances and the improvement of the spalling resistance tends to be negated when it exceeds 10 mm. The purity of the aragonite-type calcium carbonate is preferably 80% or more. Low melting-point minerals are produced and the refractory property of the brick declines when this purity is low.

The refractory of the present invention is produced by combining aragonite-type calcium carbonate as needed with the refractory aggregate raw material, adding known nonaqueous binders such as tar, liquid phenol resin, polyurethane, polypropylene, and wax (usually in a quantity of about 1-5 parts per 100 parts of the refractory aggregate) by the usual method, kneading, molding, and calcining. There is no particular specification as to the process from the addition of the nonaqueous binder up to calcining because it is carried out by the usual methods, but it is preferable to conduct calcining at about 1600-1700°C.

## Merits of the invention

The present invention obtains a magnesia-calcia-based refractory with better spalling resistance and thermal impact resistance than known magnesia-calcia-based refractories. The other properties such as the strength of the refractory of the present invention are also as good as or better than those of conventional products. The refractory of the present invention can be used appropriately, for example, as a lining refractory for various types of furnaces.

## Practical Examples

The characteristics of the present invention are clarified further below through comparative and practical examples.

Practical Examples 1-4 and Comparative Examples 1-3

The raw materials were combined in the proportions (parts) shown in Table 1, 2 parts of polypropylene were added as binder per 100 parts of said composition, kneaded, formed into the usual shape, and calcined at 1650°C.

Spherical particles selected out from natural magnesia clinker and natural dolomite clinker (MgO content 40% and CaO content 60%) were used as the spherical particles. Natural magnesia clinker and natural dolomite clinker were used as the non-spherical particles.

The refractories obtained were examined by the following methods.

Porosity (%): according to JIS R-2205.

Bulk specific gravity: according to JIS R-2205.

Compression strength (kgf/cm$^2$): according to JIS R-2206

Flexural strength (kgf/cm$^2$, 1400°C): according to JIS R-2213.

Spalling resistance: The refractory was inserted into an electric furnace kept at 1200°C, a cycle of 15 minutes heating, 15 minutes cooling repeated, and the number of cycles until the refractory detached was studied.

The results are shown in Table 2.

Table 1.

| Raw material | Particle diameter | Practical example | | | | Comparative example | | |
|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 1 | 2 | 3 |
| Spherical magnesia clinker | 10-5 mm | 20 | 20 | 20 | 20 | — | 10 | 20 |
| Spherical magnesia clinker | <1 mm | 40 | 40 | — | — | — | — | 40 |
| Natural magnesia clinker | 3-1 mm | — | — | — | — | 20 | 10 | — |
| Natural magnesia clinker | <1 mm | — | — | 40 | 40 | 40 | 40 | — |
| Natural dolomite clinker | 3-1 mm | 30 | 30 | 30 | 30 | 30 | 30 | — |
| Natural dolomite clinker | <1 mm | 10 | 10 | 10 | 10 | 10 | 10 | — |
| Aragonite-type calcium carbonate | 3-1 mm | — | 1 | — | 1 | — | — | — |
| Spherical dolomite clinker | 10-5 mm | — | — | — | — | — | — | 30 |
| Spherical dolomite clinker | <1 mm | — | — | — | — | — | — | 10 |

Table 2.

| | Practical example | | | | Comparative example | | |
|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 1 | 2 | 3 |
| Porosity (%) | 15.9 | 17.1 | 15.8 | 16.9 | 16.4 | 16.5 | 18.0 |
| Bulk specific gravity | 2.88 | 2.91 | 2.88 | 2.90 | 2.89 | 2.89 | 2.71 |
| Compression strength ($kgf/cm^2$) | 360 | 351 | 371 | 348 | 359 | 361 | 150 |
| Flexural strength ($kgf/cm^2$, 1400°C) | 66 | 48 | 63 | 53 | 54 | 55 | 28 |
| Spalling resistance | >15 | >15 | >15 | >15 | 7 | 9 | >15 |

It is evident from Table 2 that the magnesia-calcia-based refractory of the present invention had far better spalling resistance than the magnesia-calcia-based refractories that did not contain a spherical refractory aggregate raw material, and the other characteristics were also judged to be equivalent.